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Absorption Spectrum of the NO Molecule:
The $^2\Delta$ States and their Interactions

INAUGURALDISSERTATION

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Erlangung der Würde eines Doktors der Philosophie

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von

CHRISTIAN J JUNGEN

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auf Antrag der Herren Professor Dr. E. MIESCHER und Dr. K. Dressler

Basel, den 5. Juli 1966

Prof. Dr. W. HABICHT

Dekan



Curriculum vitae

Am 22. Oktober 1941 wurde ich, Christian Jungen, heimatberechtigt in Frutigen (Kanton Bern), als Sohn des Reinwald Jungen, Gymnasiallehrer in Basel, und der Alice, geb. Huber, († 1953), in Basel geboren. Im April 1952 trat ich in das Basler Humanistische Gymnasium ein und erwarb mir an dieser Schule im Frühjahr 1960 das Maturitätszeugnis. Im Sommersemester 1960 begann ich an der Universität Basel das Studium der Naturwissenschaften in den Fächern Physik, Mathematik und Chemie. Die vorliegende Arbeit entstand in den Jahren 1965 und 1966 unter der Leitung von Herrn Prof. Dr. E. Miescher. Seit dem Herbst 1964 bin ich als Assistent an der Physikalischen Anstalt der Universität angestellt.

Während meines Studiums besuchte ich die Vorlesungen und Praktika der folgenden Herren Proff. und Drs.: K. ALDER, E. BALDINGER, E. BAUMGARTNER, R. CONZELMANN, H. DAHN, S. E. DARDEN, M. EICHLER, H. ERLNMEYER, H. HUBER, P. HUBER, E. MIESCHER, P. SCHERRER.

VACUUM-ULTRAVIOLET EMISSION AND ABSORPTION SPECTRUM OF THE NO MOLECULE: THE ${}^2\Delta$ STATES AND THEIR INTERACTIONS

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ABSTRACT

The emission spectrum of NO between 1 600 and 1 400 Å has been studied with a 1-m vacuum spectrograph. It consists of the two types of mutually perturbing ${}^2\Delta$ - X ${}^2\Pi$ bands already known from the much more complex absorption spectrum: the Rydberg systems F ${}^2\Delta$ - X ${}^2\Pi$, N ${}^2\Delta$ - X ${}^2\Pi$ and the non-Rydberg system B' ${}^2\Delta$ - X ${}^2\Pi$. The interactions between the excited states of different electron configurations are of special interest. The matrix elements $H = H_{vib} \cdot H_e$ have been obtained from detailed rotational analyses, a "deperturbation" in two steps has been carried out, and constants for the deperturbed ${}^2\Delta$ states are given. With calculated overlap integrals H_{vib} , the electronic configuration interaction energy H_e is derived. "Crossing" potential energy curves have been shown to be the appropriate zero-order approximation when $H_e \ll \omega_0$. The phase of the interaction, i.e. the sign of H_e , has been deduced from the perturbed intensities of the observed bands.

1. INTRODUCTION

Ever since large vacuum spectrographs have been built, the spectrum of the NO molecule has been studied systematically. It turned out that the system of excited states of this molecule is of fundamental interest in many respects, as has been amply demonstrated by Dressler and Miescher (1965), Lagerqvist and Miescher (1966), and Miescher (1966). While these papers deal with fine-structure analysis in the *absorption* spectrum, the present paper reports results that are based to a significant degree on analyses of bands observed in *emission* in the vacuum ultraviolet. This concerns the excited ${}^2\Delta$ states of the molecule, i.e., the non-Rydberg (NR) state B' ${}^2\Delta$ and the states F ${}^2\Delta$ and N ${}^2\Delta$, which are the first members of the *nd* Rydberg (R) series. The ${}^2\Delta$ - X ${}^2\Pi$ bands appear in emission sorted out, because the ${}^2\Sigma$ and ${}^2\Pi$ levels predissociate and do not give rise to emission in the vacuum ultraviolet. The main interest is aimed at the problem of interaction between the ${}^2\Delta$ states. In the spectrum this interaction is evident as a perturbation, while a theoretical treatment of this problem has been given recently by Felenbok and Lefebvre (1966).

Miescher (1956) has observed the B' ${}^2\Delta$ - X ${}^2\Pi(v', v'')$ bands of NO for $v' = 0-5$ at high resolution and has analyzed their fine structure. Huber (1964) has studied the rotational structure of the infrared emission bands B' ${}^2\Delta$ - C ${}^2\Pi$ (4, 1) and F ${}^2\Delta$ - C ${}^2\Pi$ (0, 0) and (1, 1) as well as the structure of the visible bands B' ${}^2\Delta$ - B ${}^2\Pi$ (1, 0) and (2, 0). Jungen and Miescher (1965) have published a print of the emission spectrum of NO in the vacuum ultraviolet (1 600-1 400 Å) and have given a list of the wavelengths of the bands observed, including B' ${}^2\Delta$ - X ${}^2\Pi(v', v'')$ up to $v' = 10$, and bands of the F ${}^2\Delta$ - X ${}^2\Pi$ and N ${}^2\Delta$ - X ${}^2\Pi$ systems.

Figure 1(a) shows the emission spectrum of an uncondensed discharge through a rapidly streaming mixture of argon and nitric oxide, and Table I lists the

TABLE I
Heads of the ${}^2\Delta-X {}^2\Pi$ bands seen in Fig. 1(a) (cm^{-1})
(r, red degraded; v, violet degraded)

70 422 r	$B'-X (10, 0)$	66 811 v	$F-X (2, 0)$
69 964 v	$N-X (1, 0)$	66 790 v	
69 843 v		66 746 r	$B'-X (8, 1)$
69 518 r	$B'-X (9, 0)$	66 466 r	$B'-X (6, 0)$
68 997 v	$F-X (3, 0)$	65 811 v	$B'-X (7, 1)$
68 875 v		65 686 v	
68 621 r	$B'-X (8, 0)$	65 639 r	$B'-X (5, 0)$
67 686 v	$B'-X (7, 0)$	64 721 r	$B'-X (6, 1)$
67 562 v		64 607 r	$B'-X (4, 0)$
67 643 r	$B'-X (9, 1)$	63 490 r	$B'-X (3, 0)$

wave numbers of the band heads seen in the figure. The instrument was a 1-m vacuum spectrograph equipped with a Bausch and Lomb grating (60 000 lines/inch). Measurements of most of the rotational lines, however, originate from absorption spectra taken on plates with the 10.5-m vacuum spectrograph of the National Research Council of Canada, Ottawa, except for the bands with $v'' > 0$ and lines of high J which do not appear in the absorption of the cold gas, but which proved to be of special importance for the study of the interactions.*

2. THE ${}^2\Delta \sim {}^2\Delta$ PERTURBATION IN THE NO SPECTRUM

Figure 1(a) shows two types of bands: (i) the progression of red-degraded $B'-X {}^2\Pi (v', 0)$ bands and (ii) the somewhat weaker systems of violet-degraded $F {}^2\Delta-X {}^2\Pi (v', 0)$ and $N {}^2\Delta-X {}^2\Pi (v', v'')$ bands with a vibrational spacing about twice as large. Figure 3(a) gives potential energy curves for these states. The NR B' curve crosses the R curves F and N . These crossings produce the homogeneous perturbations in the spectrum where R and NR bands come close to each other. Positions, shapes, and intensities of these bands are altered. The branches in the perturbed bands turn over from the NR type (red-degraded) into the R type (violet-degraded) and vice versa, with one of the partners of a mutually perturbed pair appearing strengthened, the other weakened in intensity.

The system of interacting R and NR states of ${}^2\Delta$ symmetry ($F, N \sim B'$) is entirely analogous to the system of interacting ${}^2\Pi$ states ($C, K \sim B$) lying at lower energy (Lagerqvist and Miescher 1958, 1966). Its treatment in this paper, therefore, follows the "deperturbation" procedure used successfully in the case

*The wave numbers of the rotational lines of the ${}^2\Delta-X {}^2\Pi$ bands discussed in this paper may be obtained upon request as photocopies from: Depository of Unpublished Data, National Science Library, National Research Council, Ottawa, Canada.

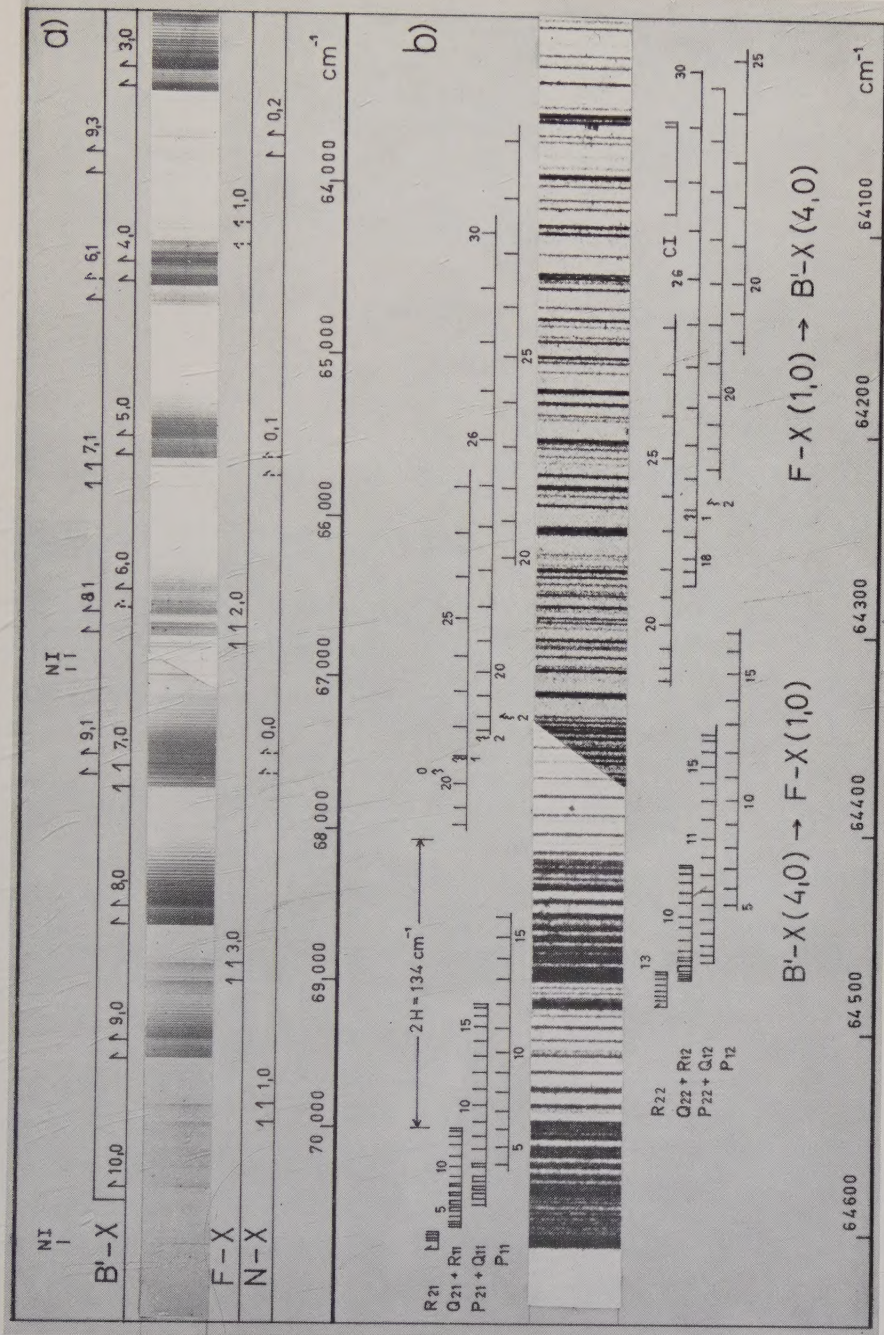


FIG. 1. (a) The emission spectrum of $^{14}\text{N}^{16}\text{O}$ 1 600–1 400 Å. (b) Enlargement showing the bands $\text{B}'\text{-X } ^2\Delta\text{-X } ^2\Pi(4, 0) \rightarrow \text{F } ^2\Delta\text{-X } ^2\Pi(1, 0)$ and $\text{F } ^2\Delta\text{-X } ^2\Pi(1, 0) \rightarrow \text{B}'\text{-X } ^2\Pi(4, 0)$. The numbers at the rotational lines are $J \rightarrow J'$.

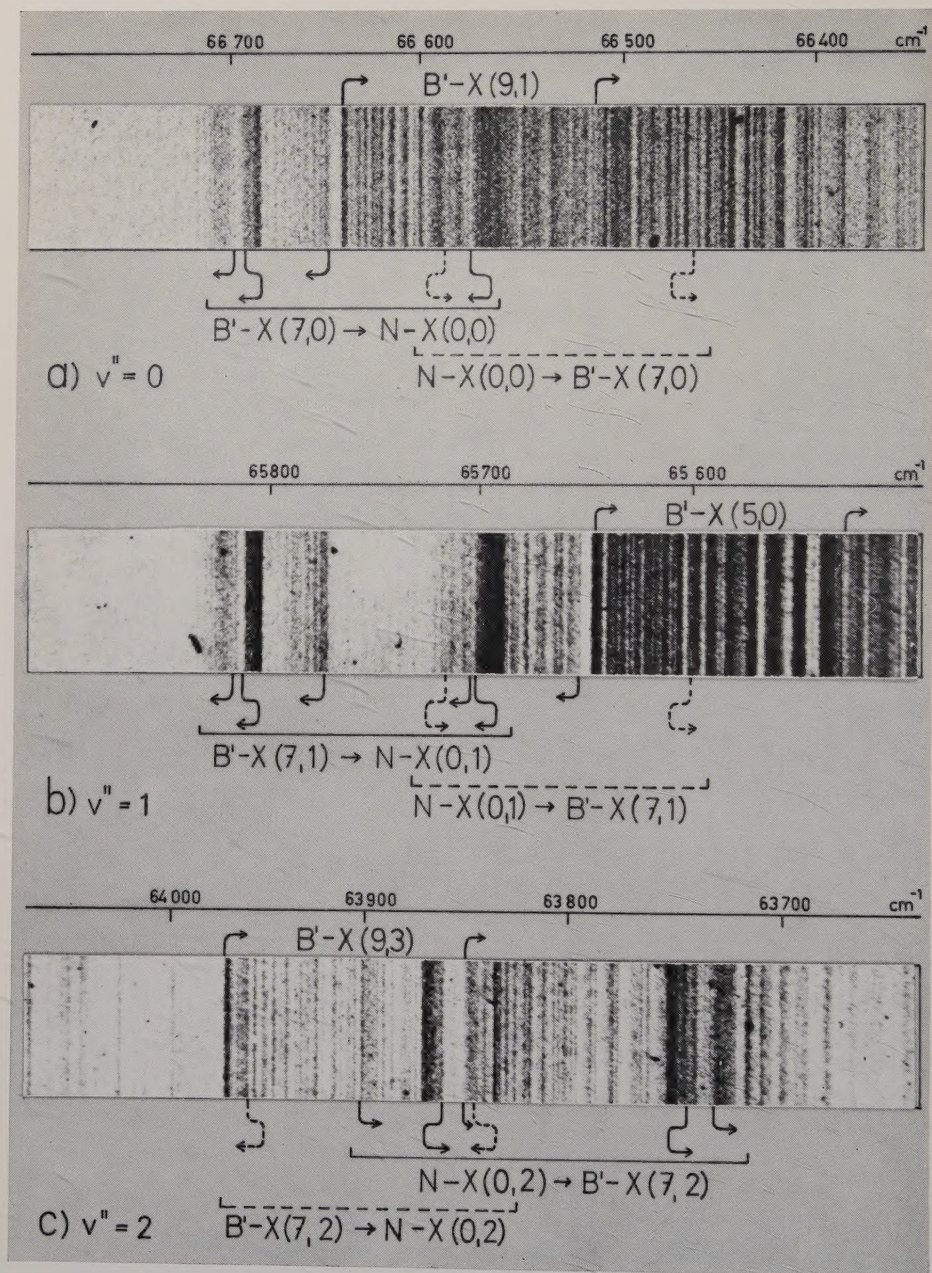


FIG. 2. The emission bands $B'^2\Delta-X^2\Pi(7, v'') \rightarrow N^2\Delta-X^2\Pi(0, v'')$ and $N^2\Delta-X^2\Pi(0, v'') \rightarrow B'^2\Delta-X^2\Pi(7, v'')$.

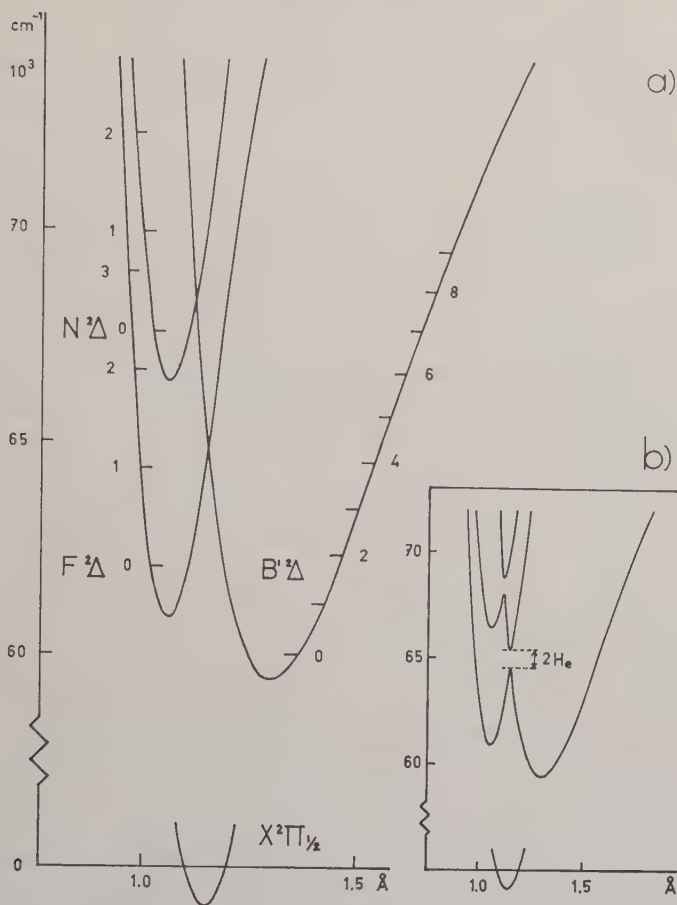


FIG. 3. Potential energy curves for the $^2\Delta$ states of NO; (a) crossing curves, (b) noncrossing curves.

of the $^2\Pi$ states. The applicability of this method will first be discussed in some detail in the following section.

3. THE CONFIGURATION INTERACTION

Excitation of the NO molecule from its ground state configuration $\sigma^2\pi^4\bar{\pi}$ ($X^2\Pi$) to either the NR configuration $\sigma\pi^4\bar{\pi}^2$ ($B'^2\Delta$) or the R configuration $\sigma^2\pi^4\delta nd$ ($F^2\Delta$, $n = 3$, $N^2\Delta$, $n = 4$) leads to the states of $^2\Delta$ symmetry which form the subject of this paper. It is well known that in the NO molecule the difference in the behavior of NR and R levels is more pronounced than in any other molecular system. However, the homogeneous perturbations observed in the spectrum result from the mixing of the two configurations, and so they disclose the limit of separability of the wave functions into pure R and NR molecular orbitals. Because in the molecule one configuration changes into the other when the internuclear distance r is adiabatically varied across the value of maximum mixing, the problem of configuration interaction is closely connected

with the problems arising from the Born–Oppenheimer approximation. In this latter approximation the wave function $\Psi_i(r, x_k)$ of the nonrotating diatomic molecule is written (electronic state i and vibrational level v) as follows:

$$(1) \quad \Psi_i(r, x_k) = \Phi_i(r, x_k) \cdot R_{i,v}(r)$$

(x_k = coordinates of electron k), neglecting the following terms in the wave equation (M = reduced mass of the nuclei)

$$(2) \quad -\frac{\hbar^2}{2M} R \frac{\partial^2 \Phi}{\partial r^2} - \frac{\hbar^2}{M} \frac{\partial R}{\partial r} \frac{\partial \Phi}{\partial r}.$$

The motion of the nuclei described by $R_{i,v}(r)$ is determined by the potential energy $E_i(r)$, which is the adiabatic energy of the molecule, given as the eigenvalue of the wave equation

$$(3) \quad -\frac{\hbar^2}{2m} \sum_k \frac{\partial^2 \Phi_i(r, x_k)}{\partial x_k^2} + V(r, x_k) \Phi_i(r, x_k) = E_i(r) \Phi_i(r, x_k)$$

(m = electron mass, V = potential energy nucleus–nucleus, nuclei–electrons, and electrons–electrons).

The problem of “crossing” or “noncrossing” arises, when, for some particular internuclear distance r_0 , two of these adiabatic potential energy curves come close to each other. It is helpful for this problem to consider the potential energy curves in terms of electron configurations. Following Weizel (1930), two limiting cases are simple, for both of which Λ , the quantum number of total electronic angular momentum along the molecular axis, is well defined:

(a) The interaction between electron configurations is so strong, that no unique assignment of the electronic wave function to a single configuration is possible, i.e., the concept of electron configuration is not applicable. In this case *no* degeneracies of states with the same Λ can occur, because only *one* quantum number, namely Λ , exists. Crossings are avoided.

(b) Individual quantum numbers can be given for each electron. A single configuration does adequately describe the electronic wave function. Degeneracies can occur and crossings are not avoided.

Actual molecules lie between the two limiting cases. The example of the NO molecule obviously is closer to case (b), in the sense that electron configurations are meaningful. However, because crossings are allowed only to the extent as these configurations are good approximations, the significance of the potential curves is slightly reduced and the possibility of separating the wave function according to equation (1) is affected. It is appropriate to divide the total potential energy $V = V^{(1)} + V^{(2)}$ into two parts, so that one of them, $V^{(1)}$, contains only the nucleus–nucleus, nuclei–electron, and the Hartree–Fock electron–electron interaction energy. If $V^{(1)}$ is substituted for V in equation (3), *crossing* potential curves result, corresponding to the limiting case (b). The configuration interaction $V^{(2)}$, which is small compared with $V^{(1)}$, then has to be added to the small perturbing terms (2). In our special case of $R \sim NR$

interaction, the factorized wave function Φ_R contains $\sigma(\delta nd)$, Φ_{NR} contains $\bar{\pi}\bar{\pi}$, that is they differ in two and only two orbitals, a case for which it is known from theory (Slater 1963) that most of the contribution to the matrix element H_e of $V^{(2)}$ arises from an integral containing only just these two orbitals. Felenbok and Lefebvre-Brion (1966) have recently calculated H_e for the ${}^2\Pi \sim {}^2\Pi$ and for the ${}^2\Delta \sim {}^2\Delta$ interactions of NO, using LCAO-MO SCF electronic wave functions. Their result in the ${}^2\Delta \sim {}^2\Delta$ case is $H_e = 300 \text{ cm}^{-1}$. The ratio of the perturbation energy H_e to the vibrational spacing is a measure of the degree to which the meaning of individual electron configurations will be lost. Since H_e for the ${}^2\Delta \sim {}^2\Delta$ system is small compared with the spacings of the vibrational levels in NR ($\omega_{NR} \approx 1\,200 \text{ cm}^{-1}$) and R states ($\omega_R = 2\,370 \text{ cm}^{-1}$), the single configuration functions Φ_R and Φ_{NR} are good approximations even in the zone $r = r_0$, and *crossing* potential energy curves E_R and E_{NR} are meaningful for the interpretation of the levels observed in the spectrum of the molecule. This provides a theoretical foundation for the method of deperturbation which has first been used in the ${}^2\Pi \sim {}^2\Pi$ case. As will be shown in the following sections, this method is the only one allowing a quantitative interpretation in the ${}^2\Delta \sim {}^2\Delta$ case as well.

If on the other hand the total potential energy $V^{(1)} + V^{(2)}$ is inserted in (3) instead of $V^{(1)}$ only, the resulting curves are of the type shown in Fig. 3(b), i.e., one curve with a double minimum and a second curve with a single minimum. At the internuclear distance $r = r_0$, the maximum of the first curve and the minimum of the second curve are separated by the energy difference $2H_e$. However, in the case where $H_e \ll \omega$, these "noncrossing" curves do not have much meaning, because the separation of the wave functions according to equation (1) does not provide a useful zero-order approximation. These curves would mean that at $r \sim r_0$ the electron configuration would have to switch from the R to the NR type and vice versa in a region of r that is small compared with the wavelength of the vibration of the nuclei, and this means that the electronic-vibration terms (2) would be large. No vibrational levels would fit into the higher curve of Fig. 2(b). H_e would have to be large compared with ω (in NO, H_e would have to be about $3\,000 \text{ cm}^{-1}$), before this curve would have any relation to observed vibrational levels.

4. THE PERTURBED VIBRATIONAL AND ROTATIONAL LEVELS

The interaction energy H between two vibrational levels, one of which belongs to the R-type, the other to the NR-type electronic state, is given in a good approximation by $H = H_{vib} \cdot H_e$, where H_e is the matrix element of the electronic interaction and H_{vib} is the overlap integral of the vibrational wave functions. Hence, the perturbation of vibrational levels will be a maximum at an energy slightly above the crossing point of the R and NR potential curves, where H_{vib} is expected to be a maximum. When H is small compared with the vibrational frequencies, as it is for the levels in NO, the perturbations can be treated in a first approximation by taking into account only the interaction in pairs between two levels R and NR which lie close to each other.

The perturbed term values $W_1'(J)$ and $W_2'(J)$ for each J are calculated from the unperturbed $W_R(J)$ and $W_{NR}(J)$ terms as the roots of the secular equation:

$$(4) \quad \begin{vmatrix} W_R - W' & H \\ H & W_{NR} - W' \end{vmatrix} = 0.$$

The interaction energy H is independent of the rotation, but the rotation changes the total energy W according to $W = T + BJ(J + 1)$. This change is different in an R and an NR level, because the rotational constants B_R and B_{NR} are unequal. Therefore W_R and W_{NR} must cross for a value $J = J_0$. In this way, the rotation of the molecule is used to test the behavior of the levels. H can be determined as

$$(5) \quad H = \frac{1}{2}|W_1'(J_0) - W_2'(J_0)|,$$

i.e., as half of the minimum distance between the perturbed $W'(J_0)$ energies at the crossing point of the unperturbed W . Figure 4 shows as an example the perturbed term curves W' (heavy lines) as well as the calculated unperturbed curves W (light lines) for the perturbation $F(v = 1) \sim B'(v = 4)$, which will be treated in detail in Section 5. Differentiation $dW'/\{d[J(J + 1)]\}$ of the curves of Fig. 4 produces the B curves of Fig. 5(a). The B values, as a consequence of the perturbation, are no longer constants; rather the B value of one of the

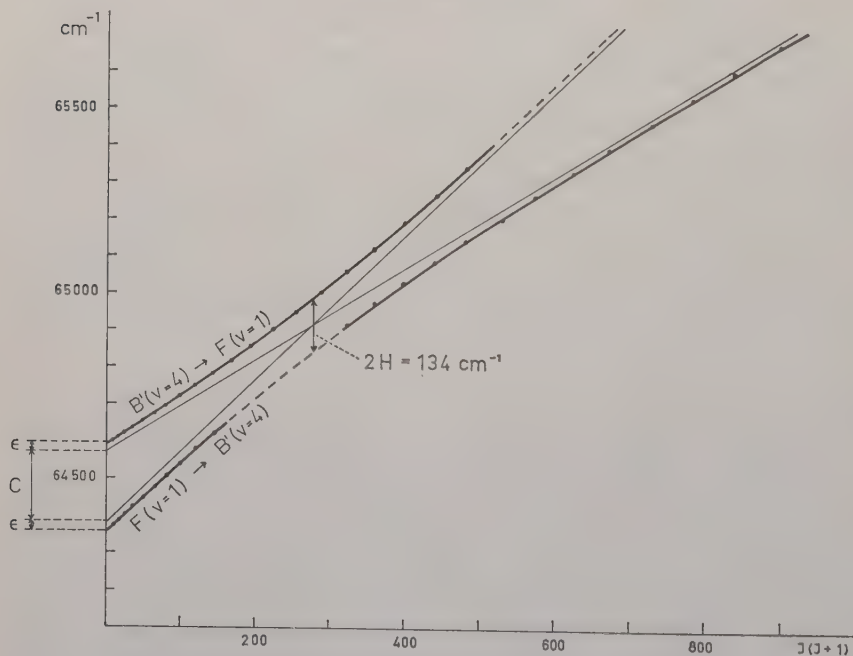


FIG. 4. $^2\Delta$ levels ($^{14}\text{N}^{16}\text{O}$) at $65\,000\text{ cm}^{-1}$. Dots connected with heavy curves represent observed energy levels. The deperturbation (1st step) of the interacting pair $F^2\Delta(v = 1) \sim B'^2\Delta(v = 4)$ yields the light lines.

perturbing levels goes over into the B value of the other. However, the mean B value is constant and the slope of the two B curves at $J = J_0$ is

$$(6) \quad \eta = \pm (B_R - B_{NR})^2 / 4H.$$

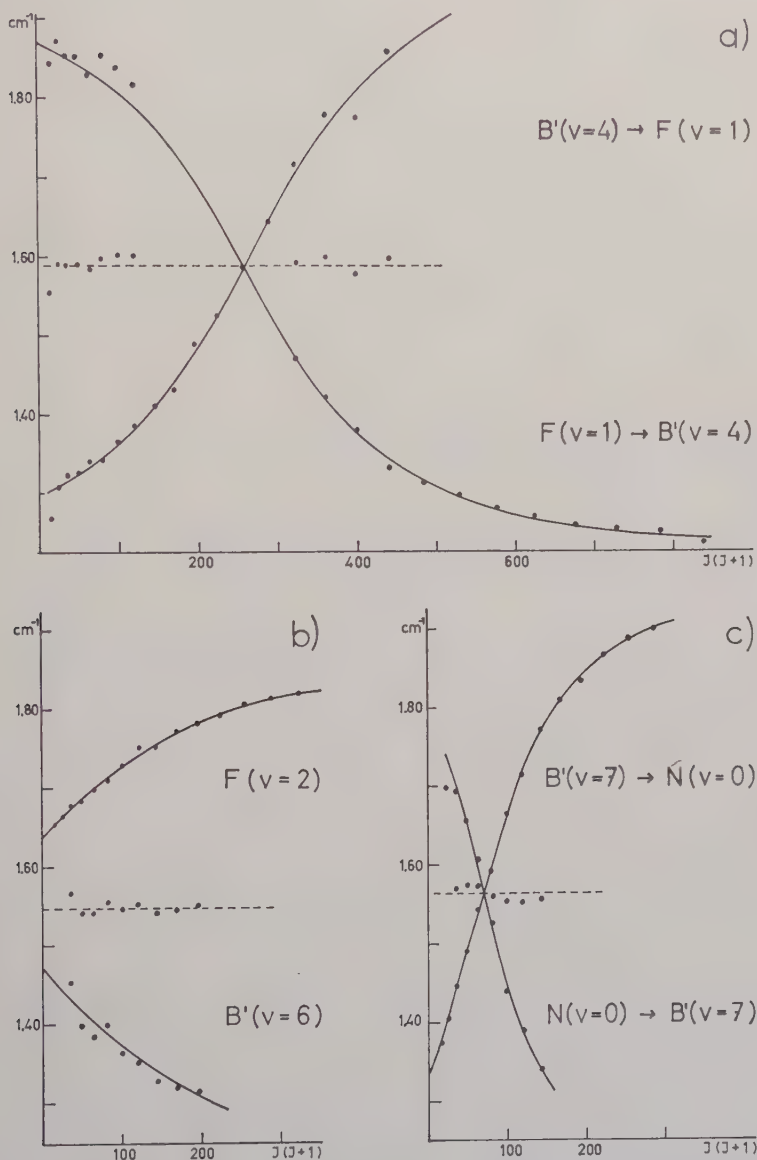


FIG. 5. Values of $B(J) = \Delta_1 W' / [2(J+1)]$ for pairs of interacting levels. The mean B value for each pair is also given.

5. DEPERTURBATION (1ST STEP)

Exactly as observed for the $C^2\Pi \sim B^2\Pi$ interaction, the perturbation $^2\Delta \sim ^2\Delta$ appears most conspicuously in the pairs of coinciding R and NR levels. These pairs are:

- (a) $F(v=0) \sim B'(v=2)$, (c) $F(v=2) \sim B'(v=6)$, and
 (b) $F(v=1) \sim B'(v=4)$, (d) $N(v=0) \sim B'(v=7)$.

If, as is the case for two of these pairs, the whole changeover of the R into the NR level and vice versa can be observed with increasing rotation, a notation already used by Dressler and Miescher (1965) is appropriate, namely $N(v=0) \rightarrow B'(v=7)$ for the level, $N-X(0, v'') \rightarrow B'-X(7, v'')$ for the band. The other interaction partner in this example is the $B'(v=7) \rightarrow N(v=0)$ level or correspondingly the $B'-X(7, v'') \rightarrow N-X(0, v'')$ band. The structure and intensity observed for the four pairs will be briefly described below, and a deperturbation in first approximation yielding the numerical results collected in Table II, will be carried out.

TABLE II
Results of the deperturbation (1st step) (cm^{-1})

1		2		3	4	5	6	7	8
<i>v</i>		<i>B</i> *							
<i>F</i> ² Δ	<i>B'</i> ² Δ	<i>F</i>	<i>B'</i>	<i>H</i>	<i>C</i>	$J_0(J_0+1)$	ϵ	H_{vib}^*	H_0
0	2	1.967	1.282	9	-317	+461	0	+0.021	430
1	4	1.942	1.236	67	-192	+272	21	+0.136	490
2	6	1.900	1.196	113	+53	-65	90	+0.253	450
3	9	1.899	1.152	<60	-536	+681	<7	+0.033	—
<i>N</i> ² Δ	<i>B'</i> ² Δ	<i>N</i>	<i>B'</i>						
0	7	1.955	1.174	45	-61	+79	24	-0.114	400

*Felenbok and Lefebvre-Brion (1966)

- (a) $F^2\Delta(v=0) \sim B'^2\Delta(v=2)$

Huber (1964) observed the perturbation in this first pair in the infrared band $F^2\Delta-C^2\Pi(0,0)$ at 10 100 Å and determined the value $H = 9 \text{ cm}^{-1}$.

- (b) $F^2\Delta(v=1) \sim B'^2\Delta(v=4)$

This pair allows observation of the complete changeover $R \rightarrow \text{NR}$ and $\text{NR} \rightarrow R$. It is as good an example as the pair $C(v=1) \sim B(v=10)$ in the $^2\Pi \sim ^2\Pi$ case. The band $B'^2\Delta-X^2\Pi(4,0) \rightarrow F^2\Delta-X^2\Pi(1,0)$ and its partner are reproduced in Fig. 1(b) from an emission spectrum taken with the 1-m vacuum spectrograph. A gap of 134 cm^{-1} is seen in all branches of the band. Taken together, the two bands appear as an interrupted and red-degraded NR band. The two observed parts are, at low J values, the beginning of the $B'-X(4,0) \rightarrow F-X(1,0)$ band and, at high J values, the end of the $F-X(1,0) \rightarrow B'-X(4,0)$ band. The gaps are marked by band heads formed by reversing branches, although the intensity drops rapidly in the violet-degraded R-type part of the

branches, where they are $F-X(1, 0)$. The absorption spectrum of cold NO gas allows, in addition, the measurement of the lines up to $J = 8\frac{1}{2}$ in the $F-X(1, 0) \rightarrow B'-X(4, 0)$ band. The positions of some of the low J lines are marked in Fig. 1(b). Term curves calculated for the means of the doublet components of the two interacting levels are plotted in Fig. 4 as functions of $J(J+1)$. The solid parts of the hyperbolas result from observed rotational lines, including a few lines measured in the infrared band $B' \ ^2\Delta-C \ ^2\Pi(4, 1)$ (Huber 1964; Jungen, Miescher, and Suter 1966). The minimum distance $2H = 134 \text{ cm}^{-1}$ at $J = J_0 = 15\frac{1}{2}$ corresponds to the gap in the branches. The levels $B'(v = 4)$ and $F(v = 1)$ are mixed 1:1 at this J value.

The B curves shown in Fig. 5(a) for the levels $B'(v = 4) \sim F(v = 1)$ result directly from the combination differences. Their mean is a horizontal line corresponding to $\frac{1}{2}(B_{F1}^* + B_{B,4}^*) = 1.589 \text{ cm}^{-1}$. Furthermore, using Lagerqvist and Miescher's method, $B_{F1}^* - B_{B,4}^* = 0.706 \text{ cm}^{-1}$ is obtained from the difference of the term curves of Fig. 4. Thus rotational constants B^* , deperturbed in first approximation, are determined for the two levels. The numerical values B^* , as well as the vibrational perturbation ϵ and the distance C between the deperturbed levels at $J = 0$, are given in Table II.

Figure 1(b) and even more clearly Fig. 4 show that the intensity distribution in the bands of this pair is somewhat asymmetric with respect to the point of maximum mixing at $J = J_0 = 15\frac{1}{2}$. The lines in the band $B'-X(4, 0) \rightarrow F-X(1, 0)$ are observed to extend beyond J_0 up to $J = 18\frac{1}{2}$, whereas the lines of the band $F-X(1, 0) \rightarrow B'-X(4, 0)$ are not observable below $J = 17\frac{1}{2}$. The theoretical interpretation of this behavior will be discussed in Section 9.

(c) $F^2\Delta(v = 2) \sim B'^2\Delta(v = 6)$

In this pair the bands do not cross because the R level lies above the NR level. The mutual perturbation is revealed prominently through anomalous intensities. The $F-X(2, 0)$ band appears strong in absorption and emission; however, the lines of high J show a sudden drop in intensity, such that in emission (see Fig. 1(a)) the impression of a breaking off is created. The $B'-X(6, 0)$ band, on the other hand, is so weak in the absorption spectrum that Dressler and Miescher (1965) were unable to identify it in $^{14}\text{N}^{16}\text{O}$. In emission the band is overlapped by $B'-X(8, 1)$ (see Fig. 1(a)), but the second component $B'-X \ ^2\Pi_{3/2}$ could be measured and thus confirm that the branches are very weak at low J . Contrary to (6, 0), the band (6, 1) is strong, as can be seen in Fig. 1(a). From measurements on the emission plates obtained with the 1-m instrument, it was possible to obtain sufficient data for the calculation of term curves for $B'(v = 6)$ and for a plot of the B curves for both levels of the pair $F(v = 2) \sim B'(v = 6)$ (Fig. 5(b)). Rotational lines measured by Shaw (1956) in the infrared rotation-vibration band 1-0 had to be used for the reduction of the (6, 1) band data. The B curves of Fig. 5(b) would cross at a complex value of J_0 which is not observable, yet it is obvious from the plot that, according to equation (6), the H value for this pair is larger than that for the pair of Fig. 5(a). The numerical data H , ϵ , C , and B^* for $F(v = 2)$ and $B'(v = 6)$ in Table II were obtained, using the same method of deperturbation as indicated in Section 5(b).

$$(d) N^2\Delta(v=0) \sim B'^2\Delta(v=7)$$

In this pair the level $v=0$ of $N^2\Delta$, the second state in the $^2\Delta$ Rydberg series, takes the role of the R level. The "crossing point" J_0 occurs at an observable J value because the NR level lies above the R level at $J=0$. Again in this case, Dressler and Miescher (1965) could identify only *one* partner of the pair in the absorption spectrum, namely $B'-X(7,0) \rightarrow N-X(0,0)$, while the other partner, $N-X(0,0) \rightarrow B'-X(7,0)$, remained hidden in overlapping structures because of low intensity. This weak band is overlapped in the emission spectrum also (by $B'-X(9,1)$, see Fig. 2(a)), but in emission the corresponding pair with $v''=1$ can be seen clearly (Fig. 2(b)), and also the pair with $v''=2$ is only slightly overlapped (by $B'-X(9,3)$, see Fig. 2(c)). $B'-X(7,1) \rightarrow N-X(0,1)$ is strong, $N-X(0,1) \rightarrow B'-X(7,1)$ is weak. The intensities for $v''=2$ are just the opposite: $B'-X(7,2) \rightarrow N-X(0,2)$, though hardly overlapped, is not visible at all. $N-X(0,2) \rightarrow B'-X(7,2)$, however, is strong and a partial rotational analysis could be carried out. Therefore, enough data for both the levels $B'(v=7) \rightarrow N(v=0)$ and $N(v=0) \rightarrow B'(v=7)$ are available for the deperturbation calculations, as they were for the $F \sim B'$ pairs discussed above. The B curves are given in Fig. 5(c) and the numerical results in Table II. The magnitude of the interaction energy $2H$ appears in the spectra of Fig. 2 directly as the interval between conspicuous heads formed in Q branches.

$F^2\Delta(v=3) \sim B'^2\Delta(v=9)$ is entered in Table II as a further pair of interacting levels, although, with its large C value, it does not form a pair in the sense of the foregoing examples. The bands corresponding to these levels appear unperturbed in the spectrum. The crossing is calculated to take place at $J_0 = 25\frac{1}{2}$, too high for observation. Nevertheless, the $B'-X(9,0)$ band can be measured and analyzed in the emission spectrum up to high rotation. It turns out that no deviation from the unperturbed values can be noticed, even for rotational lines ($J \leq 19\frac{1}{2}$), which come as close as 220 cm^{-1} to the lines of the same J of the $F-X(3,0)$ band. From this an upper limit $H < 60 \text{ cm}^{-1}$ can be derived for this pair, a value that is substantially smaller than the one for the preceding pair in the $F \sim B'$ series. Thus the maximum of interaction occurs for $F(v=2) \sim B'(v=6)$.

6. DEPERTURBATION (2nd STEP)

Having treated (Section 5) the homogeneous perturbation as if interactions would occur only between pairs of levels lying close together, we now proceed in a second step to take into account the interactions between distant levels. The method used again follows Lagerqvist and Miescher (1958), except that the matrix elements $H = H_{\text{vib}} \cdot H_e$ were obtained from calculated* vibrational overlap integrals H_{vib} and from the H_e values of Table II. The second-order corrections to be applied to the term values and to the rotational constants are sums over the interactions between the vibrational levels with the exception of those already allowed for in first order. The following levels were included: for $B'^2\Delta$ the levels $v=0$ up to 10, for $F^2\Delta$, $v=0-3$, for $N^2\Delta$, $v=0-2$. Higher levels

*It is gratefully acknowledged that Mme Lefebvre (Paris) has kindly supplied the calculated H_{vib} for $^{14}\text{N}^{16}\text{O}$ as well as for the heavier isotopes (see Section 7).

could not be identified in the spectrum, because additional perturbations, produced by yet unknown states, set in. The levels could have been extrapolated, but would not have contributed significant corrections for the $B' \, ^2\Delta$ and $F \, ^2\Delta$ levels. Regarding $N \, ^2\Delta$ see below.

Table III presents the final deperturbed term values in column 2. Figure 6

TABLE III

Deperturbed constants of the $^2\Delta$ levels for three isotopes (cm^{-1}). ($T(v)$, deperturbed term value above $X \, ^2\Pi(v = 0, J = \frac{1}{2})$, mean of the doublet components and extrapolated to $J = 0$; B_v , deperturbed rotational constant; A_v , spin-orbit coupling constant)

1	2	3	4	5	6	7	8
	$^{14}\text{N}^{16}\text{O}$			$^{15}\text{N}^{16}\text{O}$		$^{14}\text{N}^{18}\text{O}$	
$B' \, ^2\Delta$ v	$T(v)$	B_v	A_v	$T(v)$	B_v	$T(v)$	B_v
0	60 019	1.321	-2.2	60 027	1.277	—	—
1	61 204	1.302	-2.4	—	—	—	—
2	62 360	1.281	-2.5	62 326	1.237	—	—
3	63 483	1.255	-3.0	—	—	—	—
4	64 579	1.234	-3.2	64 507	1.193	—	—
5	65 640	1.214	-3.4	65 552	1.174	65 511	1.152
6	66 667	1.192	-3.7	66 568	1.153	66 519	1.131
7	67 658	1.162	-4.0	67 545	1.122	67 493	1.109
8	68 608	1.137	-4.4	68 482	1.103	68 423	1.083
9	69 521	1.118	-4.9	69 386	1.071	69 322	1.060
$F \, ^2\Delta$							
0	62 043	1.968		62 039	1.900	—	—
1	64 392	1.949		64 349	1.880	—	—
2	66 714	1.920		66 631	1.861	66 591	1.824
3	68 985	1.905		68 860	1.844	68 804	1.813
$N \, ^2\Delta$							
0	67 608	1.960		67 603	1.895	67 600	1.862
1	69 953	1.924		69 906	1.850	69 886	1.825
2	72 267	1.909		72 181	1.847	72 142	1.809

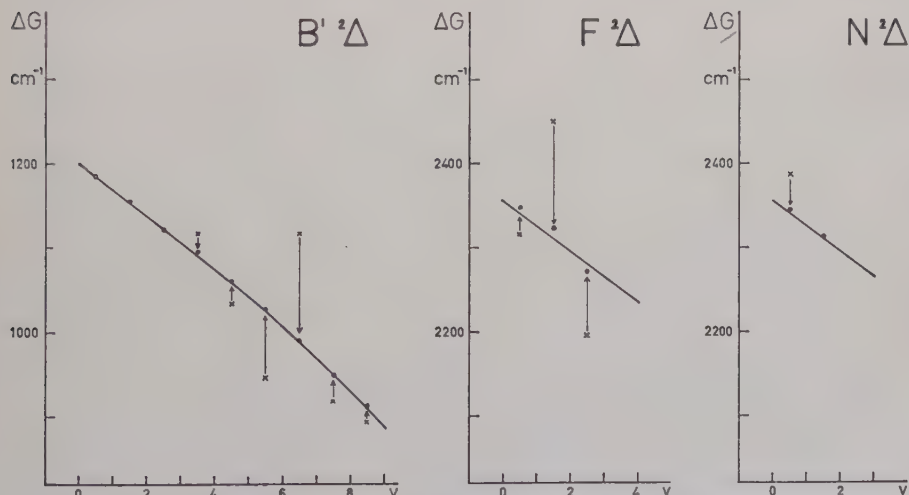


FIG. 6. $\Delta G_{v+1/2}$ curves for the states $B' \, ^2\Delta$, $F \, ^2\Delta$, and $N \, ^2\Delta$; X observed vibrational spacings, O deperturbed values.

shows for all three ${}^2\Delta$ states the vibrational spacings observed in the spectrum ($\times$) and the deperturbed $\Delta G_{v+\frac{1}{2}} = T(v+1) - T(v)$ as obtained from Table III ($\circ$). While the perturbed vibrational intervals of the $B' {}^2\Delta$ state, apart from the first ones, are irregular, the deperturbed values fit well the smooth line shown. A similar fit is obtained for the R states $F {}^2\Delta$ and $N {}^2\Delta$, for which the straight lines in Fig. 6 are drawn according to the vibrational constants $\omega_e = 2\,370\text{ cm}^{-1}$ and $\omega_e x_e = 15\text{ cm}^{-1}$, known from other Rydberg complexes of NO (Miescher 1966). Figure 7 presents the results for the perturbed and deperturbed rotational structure. The crosses ($\times$) mark B_v values for ${}^{14}\text{N}{}^{16}\text{O}$, as obtained from the line spacing observed in the spectrum at the beginning of the branches, i.e. for

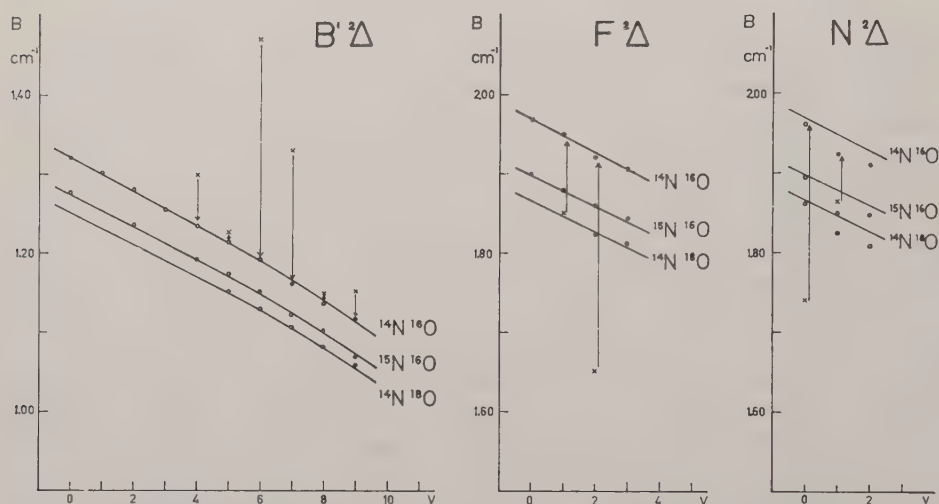


FIG. 7. B_v curves for the states $B' {}^2\Delta$, $F {}^2\Delta$, and $N {}^2\Delta$; $\times$ observed values for small J , $\circ$ deperturbed values.

small J (Fig. 5). The arrows, pointing away from the crosses in Fig. 7, are the corrections resulting from the deperturbation. They bring the deperturbed B_v values onto smooth curves. The large corrections seen for the levels of the pairs included in Table II result mainly from the first step, the much smaller corrections applied to the remaining levels stem from the second step of deperturbation. The deperturbed B_v values of the $F {}^2\Delta$ state have the magnitude expected in an R state, whereas for $N {}^2\Delta$, $v = 1$ and 2, the highest observed R levels, they are found to be somewhat too small. This unquestionably shows the influence of additional higher lying NR levels which have been neglected in the deperturbation process.

The following constants for the state $B' {}^2\Delta$ are calculated from the term values T and rotational constants B_v of Table III:

$$\begin{aligned} {}^{14}\text{N}{}^{16}\text{O} \quad B' {}^2\Delta: \quad \omega_e &= 1\,217.4\text{ cm}^{-1}, \quad \omega_e x_e = 15.61\text{ cm}^{-1}, \\ B_e &= 1.332\text{ cm}^{-1}, \quad \alpha_e = 0.021\text{ cm}^{-1}, \\ T_e &= 60\,364.2\text{ cm}^{-1}, \quad r_e = 1.302\text{ \AA}. \end{aligned}$$

These constants comprise only the levels $v = 0-6$ for which, according to Figs. 6 and 7, linear slopes are established. They differ very little from those given earlier by Miescher (1956).

For the states $F^2\Delta$ and $N^2\Delta$, using $\omega_e = 2\,370\text{ cm}^{-1}$ and $\omega_e x_e = 15\text{ cm}^{-1}$, T_e is obtained as follows:

$$F^2\Delta: T_e = 61\,823\text{ cm}^{-1},$$

$$N^2\Delta: T_e = 67\,381\text{ cm}^{-1}.$$

The accuracy of these two values is, of course, limited by the method of their derivation. The deperturbed term values T of Table III deviate not more than 10 cm^{-1} for $F^2\Delta$ and less than 5 cm^{-1} for $N^2\Delta$ from the values calculated with the constants.

The potential curves of the Morse type drawn in Fig. 3(a) illustrate the numerical values of Table III. R and NR potential curves cross each other as expected slightly below the energies of maximum H . For $F \sim B'$ this happens between the levels $v = 1$ and $v = 2$ of the Rydberg state, for $N \sim B'$ already between $v = 0$ and $v = 1$. The observation of almost unperturbed vibrational levels at energies above the crossings confirms the significance of crossing of potential curves assigned to the different R and NR configurations. Curves with avoided crossings such as shown in Fig. 3(b) and discussed in Section 3, when taken individually in no way represent the observed states.

7. ISOTOPES

The absorption spectra of the various isotopes of NO differ considerably from each other. Almost no similarity is apparent in the wavelength region of strongly perturbed structure, because the coincidence of R and NR levels is greatly influenced by the isotope shifts which are unequal for R and NR levels.

The deperturbation of the isotope spectra in two steps has been carried out for $^{15}\text{N}^{16}\text{O}$ and $^{14}\text{N}^{18}\text{O}$, but only in the regions of violent perturbations. H values obtained from mutually interacting pairs differ from isotope to isotope by not more than a few cm^{-1} , which is in agreement with the small differences between the corresponding overlap integrals H_{vib} . Consequently, the second step of the deperturbation of the isotopes was performed on the basis of the values H_e of Table II, obtained for $^{14}\text{N}^{16}\text{O}$, in combination with H_{vib} values available from Mme Lefebvre's calculations (see Section 6).

The numerical results of the final deperturbation for $^{15}\text{N}^{16}\text{O}$ and $^{14}\text{N}^{18}\text{O}$ are given in columns 5-8 of Table III. The curves of Fig. 8 represent theoretical isotope shifts $\Delta^1\nu = G(v) - G^1(v) - \Delta^1G(0)$ for the levels of the states $B'^2\Delta$, $F^2\Delta$, and $N^2\Delta$. They are calculated with the isotope factors $\rho = 0.982\,1$ for $^{15}\text{N}^{16}\text{O}$ and $\rho = 0.973\,7$ for $^{14}\text{N}^{18}\text{O}$ respectively, and with $G(v) = \omega_e(v + \frac{1}{2}) - \omega_e x_e(v + \frac{1}{2})^2$. $\Delta^1G(0)$ is the isotope shift of the lowest rotational level of the ground state $X^2\Pi(v = 0, J = \frac{1}{2})$, which amounts to 17 cm^{-1} for $^{15}\text{N}^{16}\text{O}$ and to 25 cm^{-1} for $^{14}\text{N}^{18}\text{O}$. The shifts observed in the spectra are marked as crosses ($\times$) in Fig. 8. For strongly perturbed bands these crosses do not fall on the theoretical curves. The deperturbed $\Delta^1\nu = T(v) - T^1(v)$ calculated from Table III, however, fit the curves precisely and, hence, demonstrate the success of the

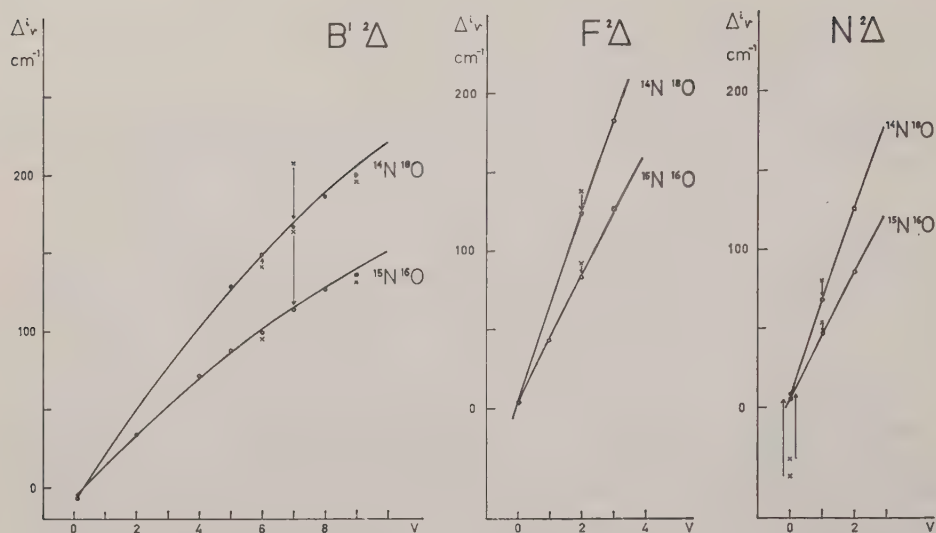


FIG. 8. Observed (X) and deperturbed (O) isotope shifts $\Delta\nu$ for the levels of the states $B' \ ^2\Delta$, $F' \ ^2\Delta$, and $N \ ^2\Delta$.

deperturbation executed here. Small deviations of a few cm^{-1} remain solely for the high levels B' , $v = 8$ and 9. Another test using the rotational constants B_v , is shown in Fig. 7. Again the deperturbed values from Table III (O) follow the theoretical curves precisely.

8. DOUBLET SPLITTING

The $^2\Delta$ states of NO and their interactions have been discussed in the preceding sections, without taking into account the influence of electron spin. According to Mulliken (1932), only a small spin-orbit coupling constant is to be expected for the $B' \ ^2\Delta$ state, because in its configuration the spin angular momentum $S = \frac{1}{2}$ is contributed entirely by the $x\sigma$ electron, which in turn contributes no orbital momentum. The doublet splitting observed in all $B'-X$ bands is indeed small, and the presence of the rotational lines $R_{21}(\frac{1}{2})$, $Q_{21}(1\frac{1}{2})$, and $P_{21}(2\frac{1}{2})$, definitely established in several bands, proves that the state $B' \ ^2\Delta$ is inverted. The same conclusion also follows from the intensity distribution within the rotational structure: for small J , in accordance with the selection rule $\Delta\Sigma = 0$, the branches R_{21} , Q_{21} , P_{21} and R_{12} , Q_{12} , P_{12} are the stronger ones; for high J , however, in accordance with the rule $\Delta J = \Delta N$, the branches R_{11} , Q_{11} , P_{11} and R_{22} , Q_{22} , P_{22} are stronger. This shift in intensity characterizes the combination of an inverted with a regular state.

The coupling constants A_v for the nearly unperturbed levels $v = 0-3, 5, 8$, and 9 of $B' \ ^2\Delta$ were determined according to Hill-Van Vleck from the observed differences $\delta = F_2(J) - F_1(J)$ of the rotational terms of the two doublet components by the formula

$$(7) \quad \delta^2 = [F_2(J) - F_1(J)]^2 = 4B_v^2[(J + \frac{1}{2})^2 + Y_v(Y_v - 4)].$$

The intercept of the straight lines with the ordinate axis, obtained by plotting δ^2 as a function of $(J + \frac{1}{2})^2$, gives $4B_v{}^2Y_v(Y_v - 4)$, hence also $A_v = B_vY_v$. A_v plotted versus v in Fig. 9 shows a rapidly rising curve.

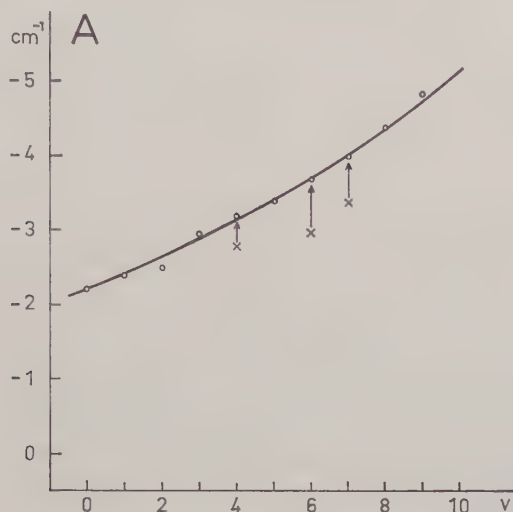


FIG. 9. Spin-orbit coupling constants A of the $B'{}^2\Delta$ vibrational levels.

The Rydberg states would be expected to belong to Hund's case b , that is to have $A = 0$. However, only $F^2\Delta$, $v = 0$ and 3 and $N^2\Delta$, $v = 2$, the least perturbed levels, lack a doublet splitting. All other ${}^2\Delta$ R levels, being partners in the pairs $F(v = 1) \sim B'(v = 4)$, $F(v = 2) \sim B'(v = 6)$ and $N(v = 0) \sim B'(v = 7)$, as well as $N(v = 1)$ show an anomalous doublet splitting. The low J lines of equal N' in the perturbed R bands clearly display an inverted splitting, and the splittings in the pertinent NR bands do not follow equation (7). When the splittings observed for the lowest J values are taken as A_v values (crosses in Fig. 9), they are too small and interrupt the regular increase of A_v with v at $v = 4, 6$, and 7. They are obviously perturbed.

Deperturbed A_v values for these levels can be obtained in the following way: by taking the sum $\delta_R + \delta_{NR}$ of the observed doublet splittings of lines with equal J , the homogeneous perturbation is eliminated. This sum can be considered, at least approximately, as the sum of the unperturbed splittings and, because $A = 0$ for the R levels, the following equation holds

$$(8) \quad \delta_R + \delta_{NR} = 2B_{NR}\sqrt{(J + \tfrac{1}{2})^2 + Y_{NR}(Y_{NR} - 4)} + 2B_R(J + \tfrac{1}{2}).$$

The $A = Y_{NR}B_{NR}$ values obtained by equation (8) for the $B'{}^2\Delta$ NR levels ($\circ$ in Fig. 9) fit well into the smooth curve. This, in turn, confirms that the R states $F^2\Delta$ and $N^2\Delta$ strictly obey case b , and that the doublet splittings observed in the R levels are borrowed from the $B'{}^2\Delta$ NR levels.

Column 4 of Table III lists the numerical values of the deperturbed constants A_v of the $B'{}^2\Delta$ state in ${}^{14}\text{N}^{16}\text{O}$. It is noteworthy that A_v increases with v . Such an increase has also been found in the $B^2\Pi$ state (Lagerqvist and Miescher

1966), whereas a decrease of A_v with v is observed in the ground state $X^2\Pi$ (Olman, McNelis, and Hause 1964).

9. PERTURBED INTENSITIES

(a) Dieke (1941) has shown that when two molecular states, 1 and 2, having equal Λ , 1 being the lower and 2 the higher, mutually interact and produce two perturbed states a and b (b lying above a), they give, in combination with a third state, bands of intensities:

$$(9) \quad I_a = \frac{1}{H^2 + w^2} (wq_2 - Hq_1)^2, \quad I_b = \frac{1}{H^2 + w^2} (wq_1 + Hq_2)^2,$$

where H is the matrix element of the interaction and can be either positive or negative. $w = |W_b - W_2| = |W_a - W_1|$ is the amount of the energy shift produced by the perturbation at the J value under consideration. q_1 and q_2 are the unperturbed transition amplitudes. $I_1 = q_1^2$ and $I_2 = q_2^2$ are the intensities of the unperturbed bands. In the present case of $R \sim NR$ interaction, the lower unperturbed state 1 for $J < J_0$ is the R state, for $J > J_0$ the NR state. The opposite holds for the higher unperturbed state 2. R and NR states cross at $J = J_0$. Therefore, we obtain

$$\text{for } J < J_0: \quad q_1 = q_R, \quad q_2 = q_{NR}$$

$$\text{for } J > J_0: \quad q_1 = q_{NR}, \quad q_2 = q_R$$

and the equations (9) can be written

$$(10) \quad \begin{aligned} I_a &= \frac{1}{H^2 + w^2} (wq_{NR} - Hq_R)^2 & \text{for } J < J_0, \\ I_b &= \frac{1}{H^2 + w^2} (wq_R + Hq_{NR})^2 \\ I_a &= \frac{1}{H^2 + w^2} (wq_R - Hq_{NR})^2 & \text{for } J > J_0, \\ I_b &= \frac{1}{H^2 + w^2} (wq_{NR} + Hq_R)^2 \end{aligned}$$

I_a belongs to the $R \rightarrow NR$ band, I_b to the $NR \rightarrow R$ band.

According to (10), one of the perturbed amplitudes is a sum, the other a difference of two terms that include the unperturbed amplitudes q_R and q_{NR} . Which of a and b is the sum and which the difference, depends upon the signs of H , q_R , and q_{NR} .

(b) When $|q_R| \approx |q_{NR}|$, i.e., when the unperturbed bands are of about equal strength, the intensity of one of the perturbed bands, according to (10), gets small for $J \approx J_0$, where $|H| \approx w$. The band pairs discussed in Section 5 have been found to be characterized by the almost complete disappearance of one of the bands in the regions of maximum interaction. Columns 3, 5, and 7 of Table IV specify which partner of the six observed pairs is weak: $I_a/I_b = 0$ means, that it is the $R \rightarrow NR$ band, the band at longer wavelengths, while $I_a/I_b = \infty$ indicates the $NR \rightarrow R$ band at shorter wavelengths. Furthermore, columns 2, 4, and 6 contain vibrational overlap integrals (see Herzberg 1950)

TABLE IV
 Mixed $^2\Delta$ levels with anomalous intensities

1	2		3	4			5			6	7
	$F(v=1) \sim B'(v=4)$			$F(v=2) \sim B'(v=6)$			$N(v=0) \sim B'(v=7)$				
v''	$q_{\text{vib}}^{\text{R}}$	$q_{\text{vib}}^{\text{NR}}$	I_a/I_b	$q_{\text{vib}}^{\text{R}}$	$q_{\text{vib}}^{\text{NR}}$	I_a/I_b	$q_{\text{vib}}^{\text{R}}$	$q_{\text{vib}}^{\text{NR}}$	I_a/I_b		
0	+0.58	+0.38	0	+0.54	+0.33	0	+0.41	-0.41	0		
1				-0.42	+0.11	∞	-0.52	+0.17	0		
2							+0.49	+0.29	∞		
H	Positive			Positive			Negative				
H_{vib}	Positive			Positive			Negative				

$$(11) \quad q_{\text{vib}}^{\text{R}} = \int \psi_v^{\text{R}} \psi_{v'}^{\text{R}} dr = \frac{1}{c} \frac{q_{\text{R}}}{R_{\text{e}}^{\text{R}}}, \quad q_{\text{vib}}^{\text{NR}} = \int \psi_v^{\text{NR}} \psi_{v'}^{\text{NR}} dr = \frac{1}{c} \frac{q_{\text{NR}}}{R_{\text{e}}^{\text{NR}}}.$$

Most q_{vib} were derived from published Franck-Condon factors (Nicholls 1964), some (including the signs of all*), had to be evaluated with oscillator functions. In (11) R_{e} is the electronic transition moment. c contains frequency and population; it is taken here as a constant factor for each R $\sim$ NR pair.

As discussed by Dressler and Miescher (1965), the intensity anomalies are responsible for the missing of the perturbed bands in the *absorption* spectrum. Yet in *emission*, two bands with the same upper levels as the missing bands appear strongly in combination with ground-state vibrational quantum numbers $v'' > 0$, namely the bands $N-X(0, 2) \rightarrow B'-X(7, 2)$ and $B'-X(6, 1)$. These emission bands gave the desired information on the missing levels (see Section 5). It can be seen in Table IV, columns 6, that $q_{\text{vib}}^{\text{R}}$ and $q_{\text{vib}}^{\text{NR}}$ for the two bands of the pair $N(v=0) \sim B'(v=7)$ have opposite signs for $v'' = 0$ and 1, but equal signs for $v'' = 2$. Therefore the level, which according to (10) combines weakly with $v'' = 0$ and 1, is strong in combination with $v'' = 2$. A similar situation holds for the bands of the pair $F(v=2) \sim B'(v=6)$ (Cf. Table IV, column 4).

The sign of H according to (10) is determined as follows: H is positive, when the a band is weak and at the same time q_{R} and q_{NR} have equal signs, or when the b band is weak and q_{R} and q_{NR} have unequal signs. H is negative, when the intensities are opposite. Table IV shows in columns 2, 4, and 6 the sign of H in the six observed pairs, determined according to these rules and provided that the phases of the R and NR electronic wave functions are chosen such that R_{e}^{R} and R_{e}^{NR} have equal sign. In addition, the sign of H_{vib} , as taken from Table II, is entered in the last row of Table IV. The comparison of the signs of H and H_{vib} leads to the interesting result that $H_{\text{e}} = H/H_{\text{vib}}$ has the same sign for both the $F \sim B'$ interaction and the $N \sim B'$ interaction.

(c) Besides the limiting case just discussed ($I_{\text{R}} \approx I_{\text{NR}}$), there is the other limiting case $I_a \approx I_b$. The first case means that the *unperturbed* R and NR bands have about equal intensities, as happens for the $^2\Delta$ levels of NO; the second assumes that the *perturbed* intensities are about equal. This case is realized for the $^2\Pi$ R and NR states of NO, for which I_{R} is known to be large

*Unfortunately, the signs of the overlap integrals are not given in the published tables of Franck-Condon factors.

compared with I_{NR} . Both examples, of course, are only approximations to the limiting cases. As a departure from the limiting case $I_{\text{R}} = I_{\text{NR}}$ or $I_a/I_b = 0$, a somewhat more detailed discussion of the problem of perturbed intensities can be pursued with the pair $F^2\Delta(v=1) \sim B'^2\Delta(v=4)$ for which the empirical data are most complete.

In the bands of this pair, one observes, on the one hand, an anomalously low intensity $I_a \ll I_b$ of the $F-X(1,0) \rightarrow B'-X(4,0)$ band near $J = 10\frac{1}{2}$, i.e., below the crossing point $J_0 = 15\frac{1}{2}$, while equal intensities $I_a = I_b$ are found near $J = 19\frac{1}{2}$, i.e., above the crossing point. From both these observations, combined with the knowledge of w and H , we can, by using equation (10), calculate the ratio of the unperturbed transition amplitudes. The result is $q_{\text{NR}}/q_{\text{R}} \approx 2$ from the first observation and ≈ 3 from the second. Furthermore, the ratio of the electronic transition amplitudes can be evaluated on the basis of the known vibrational overlap integrals (Table IV) according to $R_e^{\text{NR}}/R_e^{\text{R}} = q_{\text{NR}}/q_{\text{R}} \cdot q_{\text{vib}}^{\text{R}}/q_{\text{vib}}^{\text{NR}}$. $R_e^{\text{NR}}/R_e^{\text{R}} \approx 3-5$ is obtained. We see, therefore, that the Rydberg transition $F-X$ is considerably weaker than the non-Rydberg transition $B'-X$. In the absorption spectrum, the Rydberg bands appear only slightly weaker than the NR bands, because $q_{\text{vib}}^{\text{R}}$ is larger than $q_{\text{vib}}^{\text{NR}}$ in the pertinent range of v' values. Precise f values for the $^2\Delta-X$ $^2\Pi$ bands of NO have not yet been measured.

10. CONCLUDING REMARKS

Neither the absorption nor the emission spectrum has revealed higher vibrational levels above $v = 10$ for the $B'^2\Delta$ state. The fine structure of this last level is strongly perturbed. Dressler and Miescher (1965) and Miescher (1966), on the basis of a comparison of isotope spectra, suggested the state $U^2\Delta$, the member $n = 5$ of the δnd Rydberg series to be the partner perturbing $B'^2\Delta$ ($v = 10$). At the present time, rotational analyses, sufficient for a quantitative description of the interaction $U(v=0) \sim B'(v=10)$, have not yet been performed. The deperturbation of the $F^2\Delta$ and $N^2\Delta$ systems carried out in this paper requires only about one half of the vibrational perturbation observed in $B'(v=10)$ of $^{14}\text{N}^{16}\text{O}$, with the level $N(v=1)$ accounting for most of this amount. Thus only about 20 cm^{-1} remain as vibrational perturbation to be accounted for by the interaction $U(v=0) \sim B'(v=10)$ in $^{14}\text{N}^{16}\text{O}$.

Figure 10 presents the vibrational spacings ΔG of the $B'^2\Delta$ state plotted against the term values. The lowest possible dissociation limits $^2D + ^3P$ and $^2P + ^3P$ are indicated. As has been found for the state $G^2\Sigma^-$ of the same configuration (Lofthus and Miescher 1964), there is no convergence in $B'^2\Delta$ towards the first limit $^2D + ^3P$. Predissociation, of course, is possible above this limit, but the observations so far show neither diffuse nor sharp bands that can be assigned to the expected higher lying $^2\Delta$ levels.

The R states F and N described in this paper must be the Δ components of the nd complexes $n = 3$ and $n = 4$. It is still an unsolved problem why these Δ components are separated from the Π and Σ^+ components $H, H'(n=3)$ and $O, O'(n=4)$, and no new insight has been gained in this matter. Λ splitting, which is a sign of l decoupling, has not been observed in any $^2\Delta$ level. Recently also f complexes have been detected in the NO term system (Miescher 1966).

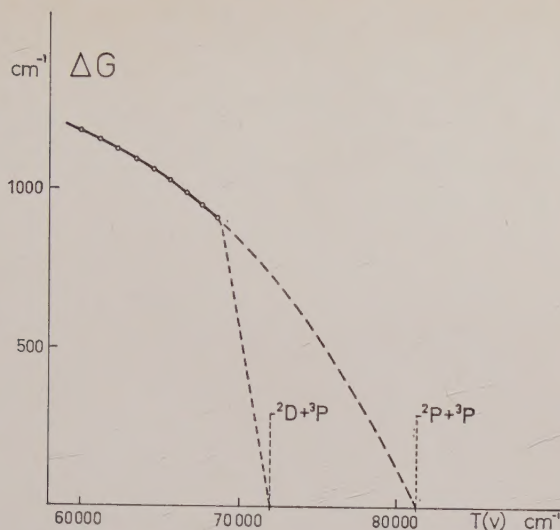


FIG. 10. Vibrational quanta ΔG as a function of the term values $T(v)$ in the state $B' \ ^2\Delta$.

$4f$ is found separated by only 190 cm^{-1} from the $4d$ complex, but its structure is not yet unraveled. The deperturbation of the $B' \ ^2\Delta$ levels below $v = 10$, requires no more than the two R states $F \ ^2\Delta$ and $N \ ^2\Delta$ of the d complexes. The absence of residual perturbations in the B' levels may be taken as an indication that the Δ component is not split off in the $4f$ complex.

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